

HEAT-CURED FURAN BINDER SYSTEM

3 Technical Field of the Invention

This invention relates to a heat-cured furan foundry binder system comprising a furan binder and a furan monomer or oligomer containing at least two terminal hydroxymethyl groups. The binders are particularly useful as warm-box binders, because they cure faster and foundry shapes (typically cores and molds) made with the binders exhibit higher tensile strengths than those made with conventional heat-cured furan binders.

10 Background of the Invention

11 Heat-cured furan binder systems are well known. Of particular interest are the so-called hot-
12 box and warm-box binder systems. Hot-box furan binders typically comprise a furan, urea
13 formaldehyde resin, and phenol formaldehyde resin. They are cured with an inorganic or
14 organic salt at temperatures of 200°C to 300°C. On the other hand, warm-box binder systems
15 are typically comprised of a furan resin and furfuryl alcohol. They are cured with an
16 inorganic or organic salt at temperatures of from about 100° C to 300° C. Examples of
17 warm-box binder systems are disclosed in U.S. Patents 4,317,763, 4,451,577, and 4,383,098.
18 These binders are preferred over hot-box binder for some applications because of their low
19 formaldehyde content, low nitrogen content, higher tensile strength, lower binder usage level,
20 availability of equipment, and the dimensional accuracy of the foundry shapes made with
21 them.

23 Recently, improvements in warm-box binders have been made. Warm-box binder systems,
24 which are nitrogen free, urea free, and essentially free of free formaldehyde, have been
25 developed. Modifications of warm-box furan binders to increase their reactivity are also
26 known. For instance, U.S. Patent 5,607,986 discloses a binder comprising a phenol
27 formaldehyde resin, modified furfuryl alcohol/formaldehyde resins, resorcinol pitch, and
28 polyvinyl acetate to improve the reactivity of the warm box system. However, further
29 improvements in these binders are still needed to improve their reactivity and the tensile
30 strengths of cores made with them.

1 U.S. Patent 6,391,942 relates furan no-bake binders comprising (a) a reactive furan resin,
2 (b) furfuryl alcohol, (c) an activator selected from the group consisting of resorcinol,
3 resorcinol pitch, and bisphenol A tar, (d) a bisphenol compound, (e) a polyol, and (f) a
4 catalyst component comprising a catalytically effective amount of a halide of a transition
5 metal. The patent discloses that the reactive furan may be a mixture of a conventional
6 reactive furan and bis-hydroxymethylfuran.

7

8 All citations referred to in this patent application are expressly incorporated by reference.

9

10 **Brief Summary of the Invention**

11 This invention relates to heat-cured furan binders comprising:

12 (a) a furan resin,

13

14 (b) furfuryl alcohol, and

15

16 (c) a furan monomer or oligomer containing at least two terminal
17 hydroxymethyl groups, preferably a methyolated furan selected from
18 the group consisting of di-methyolated furan, derivatives of di-
19 methyolated furan, polymers of di-methyolated furan, and mixtures
20 thereof, most preferably oligomers of bis-hydroxymethyl furan that
21 contain at least 50% dimers thereof.

22

23 The binders can be used in warm-box and hot-box applications. However, the binders are
24 particularly useful in warm-box applications, because they cure faster and exhibit higher
25 tensile strengths than conventional furan warm box binders. This novel aspect of the
26 invention relates to the use of methyolated furan selected from the group consisting of di-
27 methyolated furan, derivatives of di-methyolated furan, polymers of di-methyolated

1 furan, and mixtures thereof, preferably oligomers of bis-hydroxymethyl furan (BHMFO)
2 that contain at least 50% dimers thereof, in combination with the other components of the
3 heat-cured furan binder.

4

5

6 The advantages of using these binders over conventional heat-cured furan binders are as
7 follows:

8

9 (1) The cure speed of binder (as evidenced by lower dwell times) is much faster
10 than the cure speed of conventional heat-cured furan binder.

11

12 (2) The hot and cold tensile strengths of cores prepared by this invention are
13 higher earlier on than the cores prepared with conventional heat-cured furan
14 binders.

15

16 These advantages will benefit foundries, which require high productivity, because the cores
17 can be handled sooner without breaking and the cycle time for producing the cores is
18 reduced.

19

20 The advantages of the furan binder disclosed in U.S. Patent 6,391,942 relate to improved
21 casting quality. The patent, which relates to no-bake furan binders cured with an acid
22 catalyst, rather than heat-cured furan binders cured with heat and a salt of an inorganic or
23 organic curing catalyst, does not teach or suggest that the tensile strengths of cores and
24 molds, produced with the binder, are improved by the addition of BHMFO. Furthermore,
25 the patent requires that a polyol be used in the no-bake binder formulation. The subject
26 binder does not require a polyol. If a polyol is used in the binder formulation, typically the
27 amount of polyol used is less than 20 parts by weight based upon 100 parts of binder,

1 preferably less than 5 parts by weight.

2

3 The binder is used to prepare foundry shapes, e.g. molds and cores, by mixing a minor
4 amount of the binder with a major amount of foundry aggregate and a catalytically amount of
5 a latent acid curing catalyst to form a foundry mix. The foundry mixes are used to prepare
6 foundry shapes. The foundry shapes are cured in the presence of the latent acid curing
7 catalyst, preferably copper tosylate, when they are heated at temperatures of about 100 °C to
8 300 °C. The binder is cured by the application of radiant heat or heated generated by a
9 microwave.

10

11 Metal castings can be prepared from the foundry shapes by methods well known in the art.

12

13 **Detailed Description of the Invention**

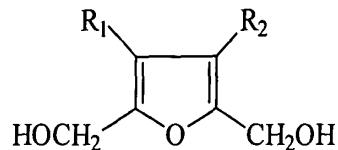
14 The detailed description and examples will illustrate specific embodiments of the invention
15 will enable one skilled in the art to practice the invention, including the best mode. It is
16 contemplated that many equivalent embodiments of the invention will be operable besides
17 these specifically disclosed. All units are in the metric system and all percentages are
18 percentages by weight unless otherwise specified.

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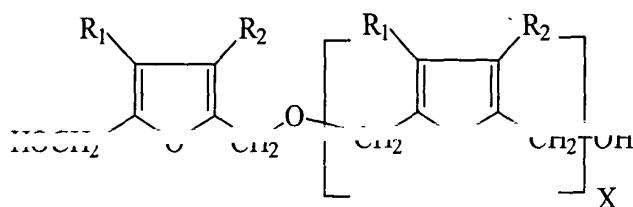
20 For purposes of this disclosure, a "warm-box binder system" is defined as a binder system
21 comprised of a furan resin and furfuryl alcohol cured with a salt of an inorganic or organic
22 acid curing catalyst at temperatures of from about 100 °C to 300 °C. Such binder systems are
23 well known in the art (see, for example, U.S. Patent 5,607,986). A "hot box binder system"
24 is defined as a binder system comprised of furan, urea formaldehyde, and phenol
25 formaldehyde, which is cured at temperatures of 200°C to 300°C using ammonium nitrate or
26 a sulfonic acid salt as curing catalysts.

27

1 The methyolated furans include di-methyolated furans having the following chemical
2 structures:



3
4
5
6 or
7



8
9
10

11 where "X = 1, and where R₁ and R₂ are hydrogens, hydroxy- methyl, alkylaral, aromatic,
12 aliphatic or a substituted aliphatic groups such as alkyl, aralkyl, cycloalkyl, alkenyl,
13 aralkenyl, alkynyl, aralkynyl, derivatives of di-methyolated furan, polymers of di-
14 methyolated furan, and mixtures thereof, preferably oligomers of bis-hydroxymethyl furan
15 that contain at least 50% dimers thereof.

16

17 Reactive furan resins that can be used in the process are preferably low nitrogen furan resins.
18 The furan resins are prepared by the homopolymerization of furfuryl alcohol in the presence
19 of heat, according to methods well-known in the art. The reaction temperature used in

1 making the furan resins typically ranges from 95°C to 105°C.

2

3 Preferably, the furan binder is a low nitrogen, modified-furan binder, which cures with a
4 latent acid curing catalyst at temperatures of from about 100 °C to 300 °C. For purposes of
5 this disclosure, a "modified furan resin" is a furan resin which is made from furfuryl alcohol,
6 urea formaldehyde oligomers, and formaldehyde at elevated temperatures under essentially
7 acidic conditions at a pH of from 5.0 to 6.0, preferably 5.0 to 5.5. The weight percent of
8 furfuryl alcohol used in making the nitrogen free modified furan resins ranges from 50 to 65
9 percent; the weight percent of the urea formaldehyde used in making the low nitrogen
10 modified furan resins ranges from 10 to 35 percent; and the weight percent of the
11 formaldehyde used in making the nitrogen free modified furan resins ranges from 1 to 20
12 percent, where all weight percents are based upon the total weight of the components used to
13 make the modified furan resin.

14

15 The reaction temperature used in making the modified furan resins ranges from 95 °C to 105
16 °C. The reaction is continued until the percentage of free formaldehyde is less than 3 weight
17 percent, typically from 1 to 2 weight percent. The viscosity of the resin typically ranges from
18 about 50 centipoise to 300 centipoise, and the refractive index is from 1.400 to about 1.600.

19

20 Although not necessarily preferred, urea-formaldehyde resins, phenol-formaldehyde resins,
21 novolac resins, and phenolic resole resins may be used in addition to the furan resin.

22

23 The reactive furan resin is diluted with furfuryl alcohol to reduce the viscosity of the reactive
24 furan resin and to improve the properties of the binder.

25

26 The heat-cured binders are made by combining the furan resin, furfuryl alcohol, and
27 methyloolated furan. The amounts of the components are from 5 parts by weight to 70 parts

1 by weight furan resin, preferably from 10 parts by weight to 50 parts by weight; from 5
2 parts by weight to 70 parts by weight furfuryl alcohol, preferably from 10 parts by weight
3 to 50 parts by weight; and from 5 parts by weight to 80 parts by weight methylolated furan,
4 preferably from 10 parts by weight to 50 parts by weight, based upon 100 parts by weight
5 of binder.

6

7 In general, any salt of a strong inorganic or organic acid, preferably inorganic acid,
8 typically an acid having a pH< 2, can be used as the curing catalyst. Examples of salts of
9 inorganic acids, which can be used, are ammonium chloride, ammonium sulfate,
10 ammonium nitrate, aluminum perchlorate, cupric perchlorate, and chromic perchlorate.
11 Examples of salts from organic acids include copper phenol sulfonate, aluminum toluene
12 sulfonate, zinc phenol sulfonate, and copper tosylate, and the like, most preferably copper
13 toluene sulfonate. The amount of curing catalyst used is the amount required to result in
14 foundry shapes, which can be handled without breaking. Generally, this amount is from 1
15 part to 40 parts, preferably from 10 parts by weight to 40 parts by weight, most preferably 15
16 parts by weight to 35 parts by weight, based upon 100 parts binder.

17

18 The binders are typically cured at temperatures of from 100°C to 300°C.

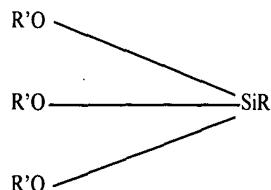
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20 Preferably, the heat-cured binder contains a silane. Examples of silanes, which can be used
21 in the binder, are represented by the following structural formula:

22

23

24



1
2 wherein R' is a hydrocarbon radical and preferably an alkyl radical of 1 to 6 carbon atoms and
3 R is an alkyl radical, an alkoxy-substituted alkyl radical, or an alkyl-amine-substituted alkyl
4 radical in which the alkyl groups have from 1 to 6 carbon atoms. The silane is typically used
5 in amounts of 0.1 part by weight to 2 parts by weight, preferably from 0.1 part by weight to
6 0.5 part by weight based upon 100 parts binder.

7
8 Examples of some commercially available silanes are Dow Corning Z6040 and Union
9 Carbide A-187 (gamma glycidoxy propyltrimethoxy silane); Union Carbide A-1100 (gamma
10 aminopropyltriethoxy silane); Union Carbide A-1120 (N-beta(aminoethyl)-gamma-amino-
11 propyltrimethoxy silane); and Union Carbide A-1160 (Ureido-silane).

12
13 The binder may contain an activator, which promotes the polymerization of furfuryl alcohol.
14 The activator a tar selected from the group consisting of resorcinol pitch, bis phenol A tar,
15 ~~and mixtures thereof~~, preferably resorcinol. Bisphenol A tar is defined as the highly viscous
16 product, which remains on the bottom of the reaction vessel after bisphenol A is produced
17 and distilled from the reaction vessel. Bisphenol A tar is a solid at room temperature and has
18 a melting point of about 70 °C to 80 °C. Bisphenol A tar is mostly dimers, trimers, and
19 polymeric bis phenol A. It may also contain substituted materials.

20
21 A mixture of bisphenol A tar and resorcinol pitch can be used to modify the binder in an
22 amount such that the ratio of bisphenol A tar to resorcinol pitch is from 3:1 to 1:3, most
23 preferably about 1:1. The bisphenol compound used is bisphenol A, B, F, G, and H, but
24 preferably is bisphenol A. The amount of bisphenol A tar used is typically from 1 part by
25 weight to 10 parts by weight based upon 100 parts of binder.

26
27 The binder may also contain polyvinyl acetate. Typically the polyvinyl acetate used has a

1 molecular weight average of from about 1,000 to about 100,000, preferably from about 5,000
2 to about 25,000. A typical viscosity of the polyvinyl acetate, in any appropriate solvent (such
3 as benzene) when required, is about 1 centipoise to about 25 centipoise, preferably about 1
4 centipoise to about 5 centipoise. The amount of polyvinyl acetate used is typically from 1
5 part by weight to 10 parts by weight based upon 100 parts of binder.

6

7 Although not required, bench life extenders may also be added to the binder formulation.
8 Examples of bench life extenders include alkaline earth metal carbonates such as magnesium
9 carbonate, calcium carbonate, and barium carbonate, and alkaline earth metal oxides such as
10 magnesium oxide, calcium oxide, and barium oxide, preferably calcium carbonate. The
11 particle size of the bench life extender typically is from about 0.5 micron to about 25
12 microns, preferably from about 1 micron to about 10 microns. It has been found that the use
13 of the bench life extender in amounts of from 0.01 to 1.0 weight percent of the thermosetting
14 resin, preferably 0.05 part by weight to 0.5 part by weight, most preferably 0.05 part by
15 weight to 0.1 part by weight, are effective. Although more bench life extender can be used,
16 this is unnecessary in most cases and only increases the cost of the binder without a
17 significant increase in benefits, and in some cases may even decrease the bench life of the
18 foundry mix.

19

20 It will be apparent to those skilled in the art that other additives such as release agents,
21 solvents, etc. can be used and may be added to the binder composition, aggregate, or foundry
22 mix.

23

24 The aggregate used to prepare the foundry mixes is that typically used in the foundry industry
25 for such purposes or any aggregate that will work for such purposes. Generally, the aggregate
26 will be sand, which contains at least 70 percent by weight silica. Other suitable aggregate
27 materials include zircon, alumina-silicate sand, chromite sand, and the like. Generally, the

1 particle size of the aggregate is such that at least 80 percent by weight of the aggregate has an
2 average particle size between 40 and 150 mesh (Tyler Screen Mesh). Typically, the weight
3 ratio of foundry aggregate to binder is from 100:1 to 100:10, preferably from 100:1 to 100:5.

4

5 Although it is possible to mix the components of the binder with the aggregate in various
6 sequences, it is preferred to add the latent acid curing acid catalyst to the aggregate and mix it
7 with the aggregate before adding the binder.

8

9 Curing is accomplished by heating the shaped foundry mix in a convection oven, a
10 microwave oven, or by means of another heat source. Generally, however, curing is
11 accomplished by injecting the foundry mix into a core box, which has been heated to a
12 temperature sufficient to cure the foundry mix and produce a workable foundry shape.
13 Generally, the temperature needed to cure the foundry mix is from 180°C to 300°C,
14 preferably from 200°C to 260°C. A workable foundry shape is one that can be handled
15 without breaking. Generally, the dwell time (the time the shaped foundry mix resides in the
16 core box) is from 15 seconds to 120 seconds, usually from 30 seconds to 90 seconds. This is
17 typically the cure time needed to produce a workable foundry shape. By using the binders of
18 this invention, the dwell time is decreased.

19

20 Metal castings can be prepared from the workable foundry shapes by methods well known in
21 the art. Molten ferrous or non-ferrous metals are poured into or around the workable shape.
22 The metal is allowed to cool and solidify, and then the casting is removed from the foundry
23 shape.

24

Abbreviations

26 The following abbreviations are used:

27

1	BAT	bisphenol A tar
2		
3	BHMFO	a mixture of bis-hydroxymethyl furan monomers, furfuryl alcohol, and di-methylolated furan, which contains at least 50% dimeric methylolated furan, supplied by Dynachem Inc.
4		
5		
6		
7	CAT	a catalyst comprising phenol sulfonic acid, urea, PVA, and water.
8		
9	FA	furfuryl alcohol.
10		
11	FR	a modified warm-box furan, which is the reaction product of a mixture of formaldehyde, urea formaldehyde, and furfuryl alcohol prepared under acidic conditions at a reflux temperature of 100 °C, such that the ratio of urea formaldehyde to furfuryl alcohol is 0.63:1.0 and the average degree of polymerization is about 3-4.
12		
13		
14		
15		
16		
17	PVA	polyvinyl acetate having a molecular weight average of about 20,000 sold by Monsanto Chemical under the GELVA tradename.
18		
19		
20	RH	relative humidity.
21		
22	RP	resorcinol pitch, which is a solid at room temperature and has a melting point of 70° to 80°C. It is mostly dimers, trimers, and polymeric resorcinol.
23		
24		
25		
26	SILANE	amino alkyl di-ethoxy silane.
27		

1

Examples

2 While the invention has been described with reference to a preferred embodiment, those
3 skilled in the art will understand that various changes may be made and equivalents may be
4 substituted for elements thereof without departing from the scope of the invention. In
5 addition, many modifications may be made to adapt a particular situation or material to the
6 teachings of the invention without departing from the essential scope thereof. Therefore, it
7 is intended that the invention not be limited to the particular embodiment disclosed as the
8 best mode contemplated for carrying out this invention, but that the invention will include
9 all embodiments falling within the scope of the appended claims. All units are in the
10 metric system and all amounts and percentages are by weight, unless otherwise expressly
11 indicated. Also, all citations referred herein are expressly incorporated herein by reference.

12

13 Sand mixes were prepared by weighing 4000 grams of sand and added the catalyst and
14 mixed for 2 minutes. Then the binder was added and mixed for 2 minutes. Finally, 2.5 g
15 of a release agent (silane/FA blend) were added and mixed for 2 minutes.

16

17 The resulting foundry mixes were forced by air blowing the mix into a standard AFS core
18 box (dog bone shape), which had been heated to a temperature of 205°C, unless otherwise
19 indicated. The tensile strengths (in psi) for various samples, after being taken from the core
20 box at specified dwell times (dwell times were 20, 30, and 40 seconds), were then measured.
21 The hot tensile measurements were taken within 10 seconds after removing the shapes from
22 the core box. The cold tensile strengths were measured at various intervals after removing
23 the shapes from the corebox.

24

25 The examples show that workable foundry shapes were formed under the conditions tested.
26 It also appeared that the foundry mixes tested had sufficient flowability.

27

Examples 1-2

(Test cores prepared with lake sand)

This shows a comparison of the hot and cold tensile strengths of test cores made with a conventional warm-box binder system (binder of Example A) with those containing BHMFO using a lake sand (Manley 1L5W sand). The binder compositions are set forth in Table I and the test results are set forth in Table II.

Table I

(Binder formulations used with lake sand)

		Example A	Example 1	Example 2
10				
11	FR	40.98	36.88	32.78
12	FA	40.98	36.88	32.79
13	Water	3.74	3.37	2.99
14	PVA	4.99	4.49	3.99
15	KP	8.99	8.09	7.19
16	Silane	0.32	0.29	0.26
17	BHMFO	----	10.00	20.00

Test Conditions

22 Sand: Manley 1L5W sand, a lake sand
 23 Binder: 1.25% B.O.S.
 24 CAT: 25% B.O.B.
 25 Temperature: \approx 205 °C

Table II
(Test results using lake sand)

4	Example	A	1	2
5	Hot Tensile Strengths (psi)			
6	Dwell time/seconds			
7				
8	20	50	72	76
9				
10	30	66	84	91
11				
12	40	79	90	100
13				
14				
15	Cold Tensile Strengths (psi)			
16				
17	20	202	254	300
18				
19	30	254	329	440
20				
21	40	322	398	433
22				

23 The data in Table II indicate that the binders of Examples 1 and 2, containing BHMFO,
24 produced test cores with higher hot and cold tensile strengths than the traditional warm box
25 system (Examples A), and that higher amounts of BHMFO in the binder resulted in higher
26 tensile strengths.

Example 3

(Test cores prepared with silica sand)

30 In this example, silica sand was used instead of Manley 1L5W lake sand. The binders
31 used were the binders of Example A (containing no BHMFO) and the binder described in
32 Table III. The test results are set forth in Table IV.

1
2 **Table III**
3 **(Binder of Example 3 used with silica sand)**

3	FR	35.49
4	FA	35.48
5	Water	1.87
6	PVA	2.50
7	RP	4.50
8	Silane	0.16
9	BHMFO	20.00
10	-----	
11		100.00
12		
13	Test Conditions	
14	Sand:	Badger 5574
15	Binder:	1.25% B.O.S.
~	C.I.T.	25/0 D.U.D.
17	Temperature:	≈ 205 °C

1

2

Table IV
(Test results using silica sand)

5

6	Example	A	3
8	Dwell Time (seconds)	Hot Tensile Strength (psi)	
10	20	116	166
11			
12	30	143	181
13			
14	40	175	224
15			
16	Dwell Time (seconds)	Cold Tensile Strength (psi)	
18	20	398	463
19			
20	30	407	444
21			
22	40	422	408
23			
24			

25 The data in Table IV indicate that the binders of Example 3, containing BHMFO, produced
26 test cores with higher hot and cold tensile strengths than the traditional warm box system
27 (Examples A) when silica sand is used as the aggregate. Furthermore, if the results of
28 Example 2 and 3 are compared, the data suggest that when silica sand is used, the tensile
29 strengths of the test cores are improved when the dwell time is the same, which indicates that
30 the cores are stronger when silica sand is used as the aggregate.

31

32

33

Example 4

4 Example 3 was repeated using Badger sand, a different type of silica sand. Several tests
5 were run using different curing times. The results are set forth in Table V.

Test Conditions

7 Sand: 5574 Badger
 8 Binder: 1.25% B.O.S.
 9 CAT: 20% B.O.B.
 10 Temperature: \approx 218 °C

	Cure Time (seconds)	Hot Tensile Strengths (psi)
12		
13		
14	Test 1	
15	Binder A	25 seconds
16	Binder of Example 3	19 seconds
17		
18	Test 2	
19	Binder A	30 seconds
20	Binder of Example 3	23 seconds
21		
22	Test 3	
23	Binder A	40 seconds
24	Binder of Example 3	33 seconds

26 These test results show that current invention can be cured 20-30% faster than the control
27 without adversely affecting the tensile strengths of the test cores made with a binder within
28 the scope of this invention. This is beneficial to foundries that need high productivity,
29 because the cure time can be reduced, yet high tensile strengths can be obtained.

1
2 All of the examples demonstrate that the subject invention outperforms a conventional
3 warm-box binder with respect to cure speed and tensile performance. These improvements
4 allow the foundry operation to be more efficient and more productive. Thus, significant
5 cost savings can be realized.